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**Dimethyl Sulfoxide Complexes of
Chromium(III), Manganese(II), Iron(III),
Nickel(II), and Copper(II) Nitrates and
Magnesium and Nickel(II) Perchlorates**

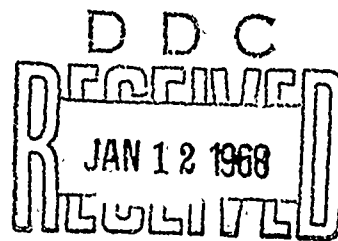
**Part 1—Preparation and Nuclear Magnetic Resonance
and Infrared Studies**

October 18, 1967



**NAVAL RESEARCH LABORATORY
Washington, D.C.**

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**Part 1—Preparation and Nuclear Magnetic Resonance
and Infrared Studies**

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October 18, 1967



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ABSTRACT

Dimethyl sulfoxide $[(CH_3)_2SO, DMSO]$ complexes of $Cr(NO_3)_3$, $Mn(NO_3)_2$, $Fe(NO_3)_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Ni(ClO_4)_2$, and $Mg(ClO_4)_2$ were prepared and investigated using infrared and nuclear magnetic resonance (nmr) spectroscopy. The infrared data indicate that the ligand forms a coordinate bond to the metal through the oxygen atom in all of the complexes, and that the tetranitrato-metal anion is present in $Mn(NO_3)_2 \cdot 3DMSO$, $Co(NO_3)_2 \cdot 3DMSO$, and $Cu(NO_3)_2 \cdot 3DMSO$. The nmr spectra of $Mn(NO_3)_2 \cdot 3DMSO$, $Co(NO_3)_2 \cdot 3DMSO$, $Ni(NO_3)_2 \cdot 4DMSO$, and $Cu(NO_3)_2 \cdot 3DMSO$ in DMSO solutions have been analyzed in terms of contact shifts, $\Delta\nu_{\text{complex}}$, and electron-nuclear hyperfine coupling constants, A_n' . The results correlate with the covalent-bond strengths of the metal atoms and fit a model for electron-spin delocalization via the σ -bond system of the complexes. Attempts to utilize liquid SO_2 as a solvent for the nmr studies were hampered by a reaction between SO_2 and the nitrate ion. Literature references to DMSO complexes and to techniques used in their study are presented in two appendixes.

PROBLEM STATUS

This is a final report on this phase of the problem; work on other phases is continuing.

AUTHORIZATION

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DIMETHYL SULFOXIDE COMPLEXES OF CHROMIUM(III), MANGANESE(II),
IRON(III), NICKEL(II), AND COPPER(II) NITRATES AND
MAGNESIUM AND NICKEL(II) PERCHLORATES

PART I - PREPARATION AND NUCLEAR MAGNETIC
RESONANCE AND INFRARED STUDIES

INTRODUCTION

The behavior of transition-metal ions in solution is associated with the chemistry of the complexes they form with the anions or with the solvent molecules; the constitution of an isolated coordination compound depends on the concentrations of the various species in the solution at the time of isolation. Since studies of the structures and thermodynamic properties of such compounds are useful in understanding the formation in solution of inorganic polymer systems which may have outstanding physical and chemical properties, NRL is investigating the reactions of transition-metal ions in solutions of selected organic ligands. One of these ligands is dimethyl sulfoxide, $(\text{CH}_3)_2\text{SO}$.

During the past few years dimethyl sulfoxide (DMSO) has received a great deal of attention from workers in medicine and chemistry because of its usefulness as a solvent. Although restrictions have been placed on widespread medical testing of this material, its chemical applications are continuing to grow. While the medicinal properties (1,2) of DMSO are not pertinent to this report, it is important to emphasize the warning given by Buckley (3) concerning the use of DMSO as a solvent in chemical operations: DMSO passes readily through all membranes tested and in many cases carries solutes through with it. Therefore, any compound which is dangerous to health by passage through the skin is potentially more hazardous in DMSO solution.

DMSO is a clear, colorless liquid which melts at 18.5°C , boils at 189°C , and has a characteristic odor (4). Its chemical reactivity has recently been reviewed (4-7). Its high dielectric constant of 48.9 makes it a good solvent for inorganic as well as organic compounds, and its electronic structure enables it to act as a donor molecule in the formation of coordination complexes with many metal salts. Literature references to DMSO complexes and to the techniques used in their study are given in the appendixes.

This report concerns preparation, nuclear magnetic resonance studies, and infrared studies of DMSO complexes of $\text{Cr}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{ClO}_4)_2$, and $\text{Mg}(\text{ClO}_4)_2$.

EXPERIMENTAL PROCEDURE

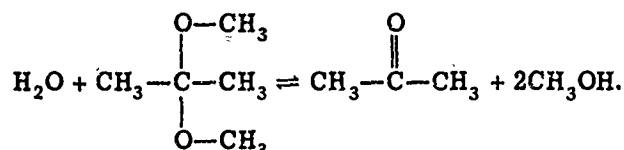
Materials Used

Reagent grade $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (as 80% aqueous solution), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, "Baker Analyzed" dimethyl sulfoxide, and Eastman Practical Grade 2,2-dimethoxypropane were used without further purification. Sulfur dioxide (Matheson Anhydrous) was purified as described below under "Liquid SO_2 Solutions."

C, H, N, S, and Cl analyses were performed by Aldridge Associates, Washington, D.C. Metal ion analyses were determined by conventional EDTA titrations (8).

Preparation of Complexes

The basic method used to prepare the complexes was as follows: Three grams of the hydrated metal salt were added to 30 ml of 2,2-dimethoxypropane, with stirring. 2,2-Dimethoxypropane reacts with water to provide an anhydrous system for formation of the complex (9):



An excess of DMSO was then added and the stirring continued. The volatiles were removed under vacuum and the final drying was made in a freeze drying apparatus.

The entire procedure was carried out in a 50-ml round-bottom flask which could be attached to the vacuum system by a glass tube fitted with standard taper joints and a stopcock. The preparations are described in greater detail below. The preparation of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$ used in this work has been described previously (10).

$\text{Cr}(\text{NO}_3)_3 \cdot 5\text{DMSO}$ — Three grams of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were stirred with 30 ml of 2,2-dimethoxypropane overnight. The solution turned deep green within 2 hours, and by morning all solid had disappeared. The solution was added to 6.4 ml of DMSO, and the mixture was stirred. Two layers formed within 1 hour; the upper layer was light green. After 2 hours of stirring the solvents were removed on a rotary evaporator and a freeze dryer.

The dark green crystals analyzed as follows:

C, 20.41%; H, 5.48%; S, 25.93%; N, 6.41%; Cr, 8.55%.

The theoretical analysis for $\text{Cr}(\text{NO}_3)_3 \cdot 5\text{DMSO}$ is:

C, 19.10%; H, 4.81%; S, 25.50%; N, 6.68%; Cr, 8.27%.

$\text{Mn}(\text{NO}_3)_2 \cdot 5\text{DMSO} \cdot \text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ — The Mn complex was particularly troublesome to prepare. The solid obtained by removing water from aqueous $\text{Mn}(\text{NO}_3)_2$ (80%) on a rotary evaporator was treated with excess 2,2-dimethoxypropane and DMSO. A portion of the light tan crystals remaining after the volatile reagents were removed under reduced pressure was used to prepare DMSO solutions for the nmr runs. This sample analyzed as $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{DMSO} \cdot \text{H}_2\text{O}$.

Analysis yielded:

C, 21.14%; H, 5.44%; S, 26.64%; N, 4.76%; Mn, 9.08%.

The theoretical analysis calculated for $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{DMSO} \cdot \text{H}_2\text{O}$ is:

C, 20.44%; H, 5.49%; S, 27.28%; N, 4.77%; Mn, 9.35%.

The remaining crystals of the monohydrated complex were placed in a freeze drying apparatus and kept under vacuum for two weeks, with periodic removal of the solid for grinding in a drybox. The resulting material analyzed as follows:

C, 17.41%; H, 4.53%; N, 6.62%; S, 23.06%; Mn, 13.20%.

The theoretical analysis for $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ is:

C, 17.44%; H, 4.39%; N, 6.78%; S, 23.27%; Mn, 13.29%.

$\text{Fe}(\text{NO}_3)_3 \cdot 6\text{DMSO}$ — Three grams of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were stirred for 18 hours in 30 ml of 2,2-dimethoxypropane. After 2 hours the initial red color of the solution had disappeared, and by the end of the stirring time the solution was yellow-green; a yellow precipitate which had formed initially was still present. DMSO (10 ml) was added and the stirring was continued for 24 hours. A yellow precipitate remained throughout the stirring. Excess reagents were removed under vacuum.

Analysis yielded:

C, 20.32%; H, 4.88%; S, 27.95%; N, 5.45%; Fe, 7.85%.

Theoretical analysis for $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{DMSO}$ is:

C, 20.28%; H, 5.11%; S, 27.07%; N, 5.92%; Fe, 7.86%.

$\text{Co}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ — Three grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to 25 ml of 2,2-dimethoxypropane in a flask fitted with a drying tube. The solution became deep purple and soon a light-colored precipitate formed as the color of the solution lightened. The precipitate remained during 7 hours of stirring. DMSO (8.8 ml) was added to the solution and the solution again turned deep purple. A new precipitate started to form before the original one had completely dissolved. (If 30 ml of DMSO are added, the precipitate will dissolve completely and no new solid will form until most of the excess DMSO is evaporated.) Removal of the volatiles on a freeze dryer left a light purple complex.

Analysis yielded:

C, 17.88%; H, 5.26%; N, 7.46%; S, 21.49%; Co, 13.78%.

Theoretical analysis for $\text{Co}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ is:

C, 17.26%; H, 4.35%; N, 6.71%; S, 23.05%; Co, 14.12%.

$\text{Ni}(\text{NO}_3)_2 \cdot 7\text{DMSO}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$ — Three grams of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were stirred with 30 ml of 2,2-dimethoxypropane for several hours. Upon the addition of 50 ml of DMSO the color of the solution changed from green to yellow-green. The precipitate observed was finer than the one which had originally formed and redissolved in the dimethoxypropane solution. The precipitate was stirred rapidly to keep it in suspension overnight. The bulk of the reagents were then removed by a rotary evaporator. A portion of the remaining solid was removed from the flask and used to prepare DMSO solutions for the nmr runs. This sample analyzed as $\text{Ni}(\text{NO}_3)_2 \cdot 7\text{DMSO}$.

Analysis yielded:

C, 23.42%; H, 5.80%; S, 29.73%; N, 3.74%; Ni, 8.12%.

Theoretical analysis calculated for $\text{Ni}(\text{NO}_3)_2 \cdot 7\text{DMSO}$ is:

C, 23.04%; H, 5.80%; S, 30.76%; N, 3.84%; Ni, 8.04%.

Additional DMSO was removed by a freeze dryer.

Analysis yielded:

C, 19.18%; H, 4.94%; S, 24.86%; N, 5.67%; Ni, 12.37%.

Theoretical analysis for $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$ is:

C, 19.40%; H, 4.88%; S, 25.90%; N, 5.66%; Ni, 11.85%.

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ — Three grams of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were stirred with 30 ml of 2,2-dimethoxypropane for 4 hours; 6.4 ml of DMSO were added slowly. A bright blue lower layer formed, and the upper layer became colorless. A small amount of ether was added but no change was apparent. The low boiling liquids were removed on a rotary evaporator. The excess DMSO was removed with a freeze dryer. The resulting light blue crystals had the following analysis:

C, 17.56%; H, 4.35%; S, 21.21%; N, 6.29%; Cu, 14.18%.

Theoretical analysis for $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ is:

C, 17.05%; H, 4.29%; S, 22.75%; N, 6.63%; Cu, 15.03%.

$\text{Ni}(\text{ClO}_4)_2 \cdot 7\text{DMSO}$ — 2.5 ml of 2,2-dimethoxypropane were added to 0.83 g of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The perchlorate dissolved endothermically, leaving a small residue of white powder which was not removed. When 2.5 ml of DMSO were added to the green solution, an exothermic reaction resulted, and a greenish-yellow precipitate formed from the resulting yellow-green solution. After further additions were made of 5 ml of 2,2-dimethoxypropane and 2.5 ml of DMSO, the flask was swirled for 3 minutes and placed on the freeze dryer. The mixture was frozen with liquid N_2 and the system degassed three times at reduced pressure. After the third degassing cycle the mixture was allowed to thaw (with system shut off from the vacuum manifold) and then refrozen with a dry ice-acetone bath. Normal freeze drying procedure was used thereafter for a total of 24 hours.

Analysis yielded:

C, 21.76%; H, 5.09%; S, 27.60%; Cl, 9.08%.

Theoretical Analysis calculated for $\text{Ni}(\text{ClO}_4)_2 \cdot 7\text{DMSO}$ is:

C, 20.90%; H, 5.26%; S, 27.90%; Cl, 8.81%.

$\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ — 0.1 ml of 2,2-dimethoxypropane was added to 33.3 mg of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ contained in an nmr tube which could be connected to a vacuum line by a stopcock assembly (Fig. 1-F); shortly after the salt had dissolved, 0.1 ml of DMSO was added. Upon addition of DMSO to the dark green solution, a light greenish-yellow precipitate started to form. An additional 0.2 ml of dimethoxypropane and 0.1 ml of DMSO were added, the tube warmed at 60°C for 1/2 minute, and then placed on the vacuum line. After several freeze-thaw degassing cycles the excess reagents were removed under vacuum, and the compound was placed on the freeze dryer for 3 days. The weight of material obtained was 54.9 mg. The theoretical yield for conversion to $\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ is 52 mg. No chemical analysis was performed.

Preparation of Solutions

DMSO Solutions — DMSO used to prepare solutions of the complexes was stored over Linde 13X Molecular Sieve for several weeks before use. All material transfers were

carried out in a drybox under a dry N_2 atmosphere. One ml of each solution was put in an nmr tube, which was capped and sealed with glyptal. For nmr spectra the DMSO contained a small amount of tetramethylsilane (TMS) to serve as an internal reference.

Liquid SO_2 Solutions — The apparatus for filling sample tubes is shown in Fig. 1. In a drybox the required amounts of complexes were loaded into nmr tubes fitted with inner 10/30 ground glass joints (K). Before removal from the drybox the sample tubes were closed with a "safety stopper" (F), which isolated the sample from the air during laboratory handling and weighing. The safety stopper, simply a vacuum stopcock with the proper ground glass joint on each end, also allowed direct attachment of the sample tube to the vacuum line after weighing.

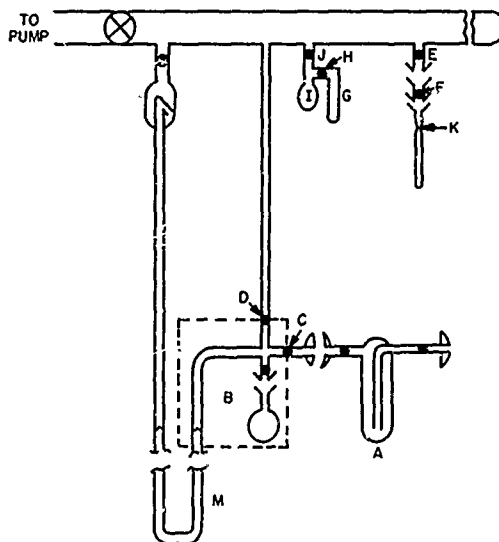


Fig. 1 - Sulfur dioxide transferring system

Sulfur dioxide was scrubbed and dried by passing the gas through a concentrated H_2SO_4 bath and through P_2O_5 suspended on glass beads. The gas was condensed in a trap (A) and cooled to $-20^\circ C$ by a NaCl-ice slush; then the filled trap was attached to the vacuum line for use as a supply of SO_2 . The correct amount of SO_2 for each sample was obtained by allowing the gas to vaporize into volume B to a preselected pressure. For flexibility in the amount of condensable vapor which could be transferred to the manifold in one operation, volume B could be varied by changing the size of the attached flask. Stopcock C was then closed, the pressure of SO_2 measured with manometer M, stopcocks D, E, and F opened, and the SO_2 condensed in the sample tube by cooling with liquid N_2 . The equilibrium pressure was recorded, stopcock F was closed, and the system was pumped out. Stopcock H was opened and TMS which had previously been condensed in volume G was allowed to vaporize to equilibrium pressure in volume G. Volume I was chosen to hold enough vapor to give approximately 5% by volume of TMS in the final sample. Stopcock H was closed, J opened, and the TMS condensed into the cooled sample tube, which was then sealed off at K. The volume of the vacuum system was calibrated by allowing TMS to vaporize into the evacuated system and recording the temperature and pressure. After the vapor was condensed into a flask and weighed, the volume of the system was calculated by assuming the ideal gas law to apply.

INSTRUMENTAL PROCEDURES

Nmr chemical shifts and line widths of the DMSO solutions were measured at 23°C using a Varian HR-100 spectrometer system. Audio sidebands, generated by a Hewlett Packard Model 200 CD oscillator and counted by a Computer Measurements Co. Model 706 BN frequency counter, were used to calibrate spectra. Chemical shift measurements are the average of 10 determinations; line widths are the average of two determinations.

The nmr spectra of the SO_2 solutions were run at 23°C on a Varian HA-100 spectrometer system, using the TMS in the solutions as a locking signal. Chemical shifts using this spectrometer were measured by counting the frequency difference between the signal channel and the lock channel for each peak of the spectrum.

Infrared spectra were run on a Perkin Elmer Model 21 or Beckman IR-5 spectrophotometer employing an NaCl prism. There were no significant differences between spectra of the complexes in KBr pellets and in mineral oil mulls. The pellets and mulls were prepared in a drybox, but no attempt was made to protect the samples from atmospheric moisture while the spectra were recorded.

RESULTS AND DISCUSSION

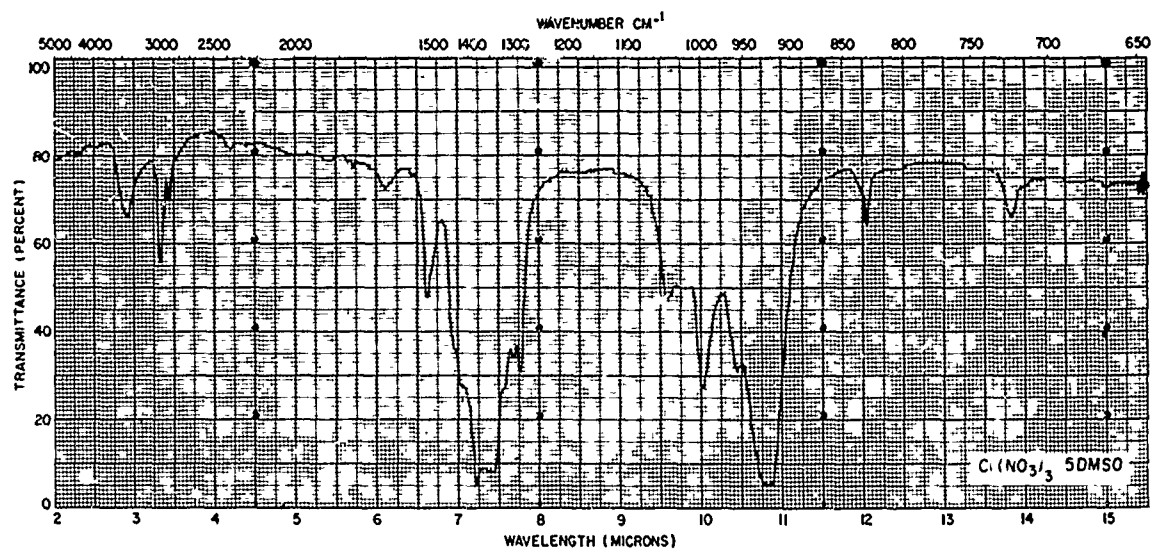
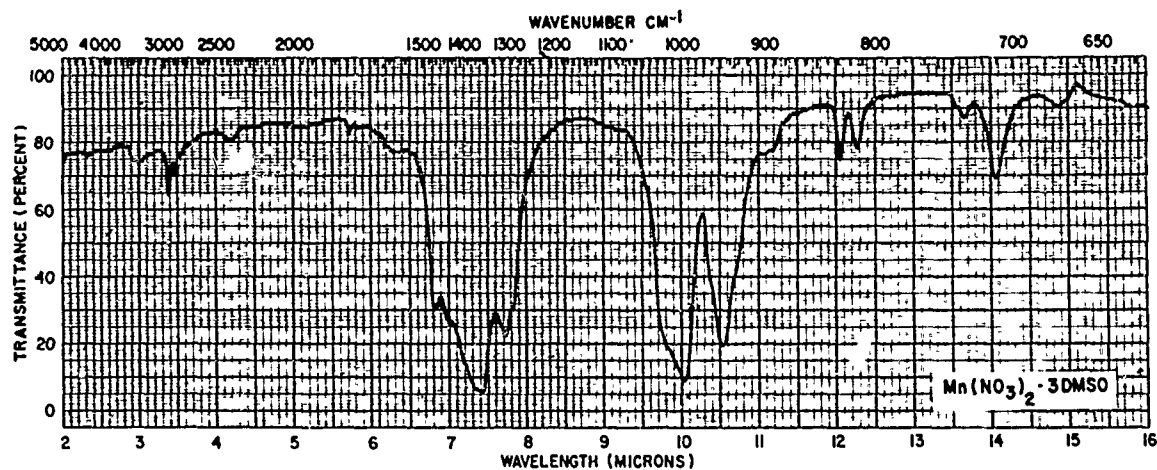
Infrared Spectroscopy

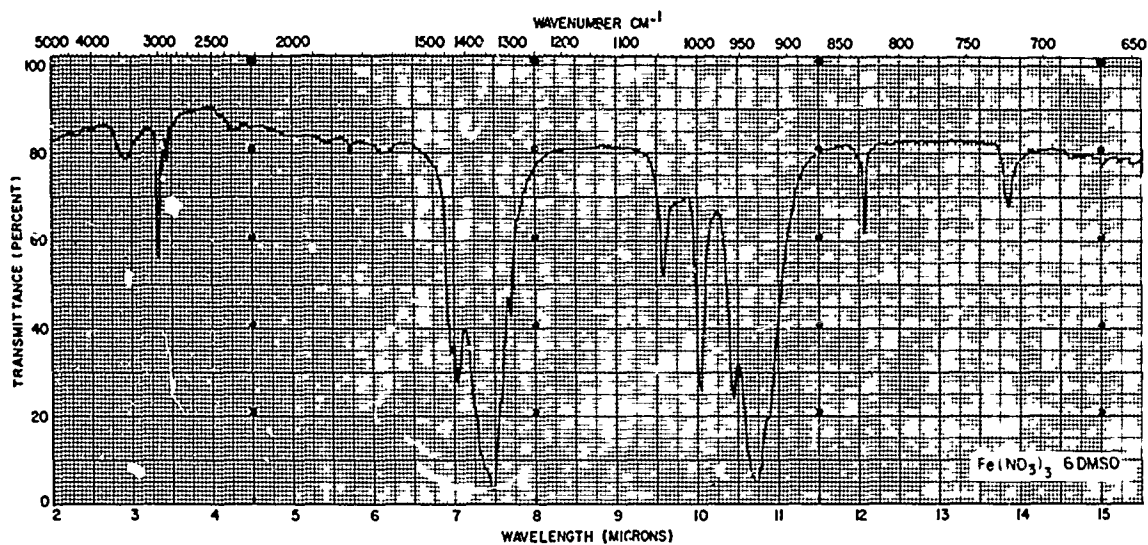
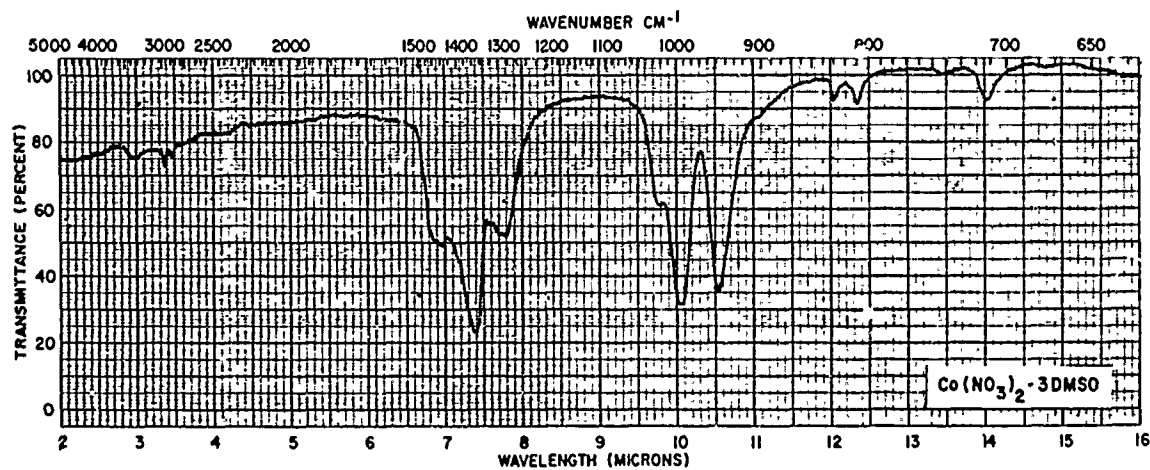
The S-O stretching frequencies in DMSO complexes compared to that in the free ligand (1055 cm^{-1}) has become the chief criterion for deciding whether DMSO forms bonds to a metal atom through the oxygen or sulfur atom. A frequency lower than that in free DMSO has been taken to indicate bonding through the oxygen atom, while a higher frequency indicates bonding through sulfur (11-13). Recent x-ray studies have given support to this interpretation of the infrared data (14).

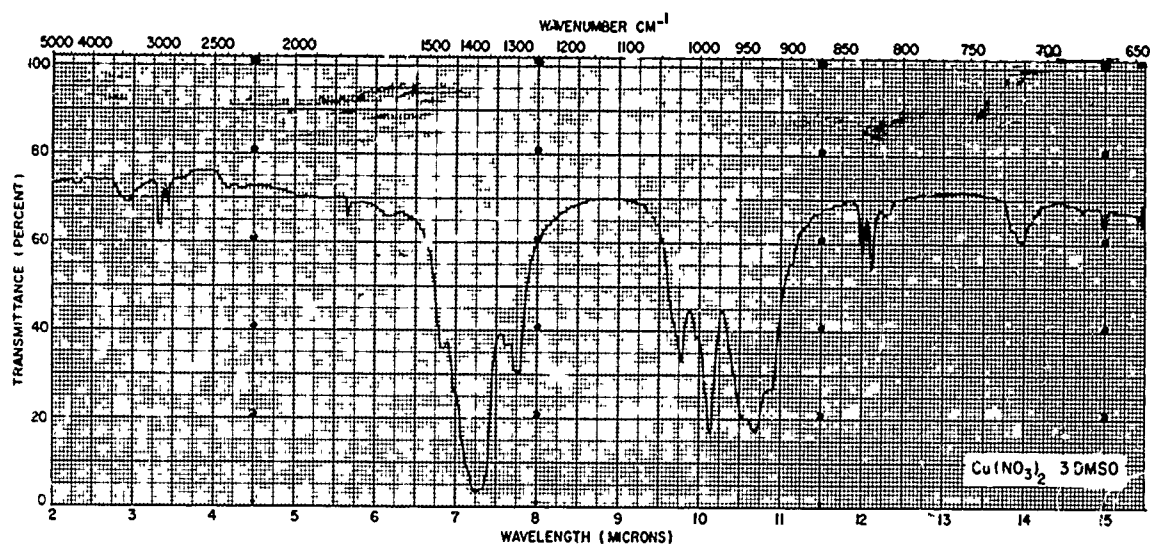
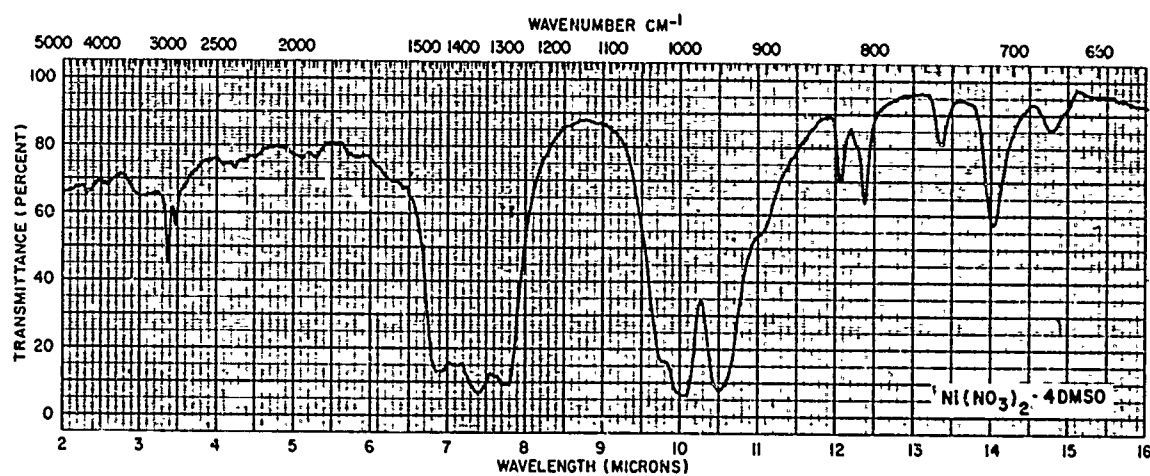
DMSO complexes of a series of chromium and manganese arene carbonyls (15,16), as well as certain complexes of metals in the second and third transition series (17-20), and in the actinide series (18,20,21), show an increased S-O stretching frequency. In the case of the arene carbonyls of chromium and manganese there is evidence that the higher frequencies observed for their S-O stretching modes are due to the formation of a sulfur-metal bond and not to some influence of the other coordinated groups upon the S-O bond, since Strohmeyer and Gultenberger (15) reported that they could not isolate any compound of the type $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}$ when L was an oxygen base or a sulfone ($\text{O}-\text{S}-\text{O}$), but could when L contained a sulfur atom with an unshared pair of electrons like DMSO. The S-O stretching frequencies are given in Appendix B for those compounds for which they have been reported.

The infrared spectra of the complexes prepared in this work are given in Figs. 2. These spectra are of solid samples in KBr pellets; no change was evident when the spectra were run as Nujol mulls. For the nitrates the absence of bands in the 1050 cm^{-1} to 1150 cm^{-1} region precludes bonding through sulfur. In the spectra of the perchlorates the band at 1090 cm^{-1} is attributable to the perchlorate ion, and again bonding occurs via oxygen. The assignment of bands in the infrared spectrum of the metal nitrate - DMSO complexes is difficult and no assignments will be attempted, since there is some disagreement about whether the 950 cm^{-1} or the 1000 cm^{-1} band should be assigned to the S-O stretching frequency (17,22).

It is also possible for the nitrate ion to act as a coordinating group in either a uni- or bidentate fashion (23,24). Table 1 lists the bands which are expected for the three modes in which the nitrate group may be present in a molecule. The chromium and iron complexes appear to contain no coordinated nitrate ion. The presence of several bands

Fig. 2a - Infrared spectrum of $\text{Cr}(\text{NO}_3)_3 \cdot 5\text{DMSO}$ Fig. 2b - Infrared spectrum of $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{DMSO}$

Fig. 2c - Infrared spectrum of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{DMSO}$ Fig. 2d - Infrared spectrum of $\text{Co}(\text{NO}_3)_2 \cdot 3\text{DMSO}$

Fig. 2e - Infrared spectrum of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ Fig. 2f - Infrared spectrum of $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$

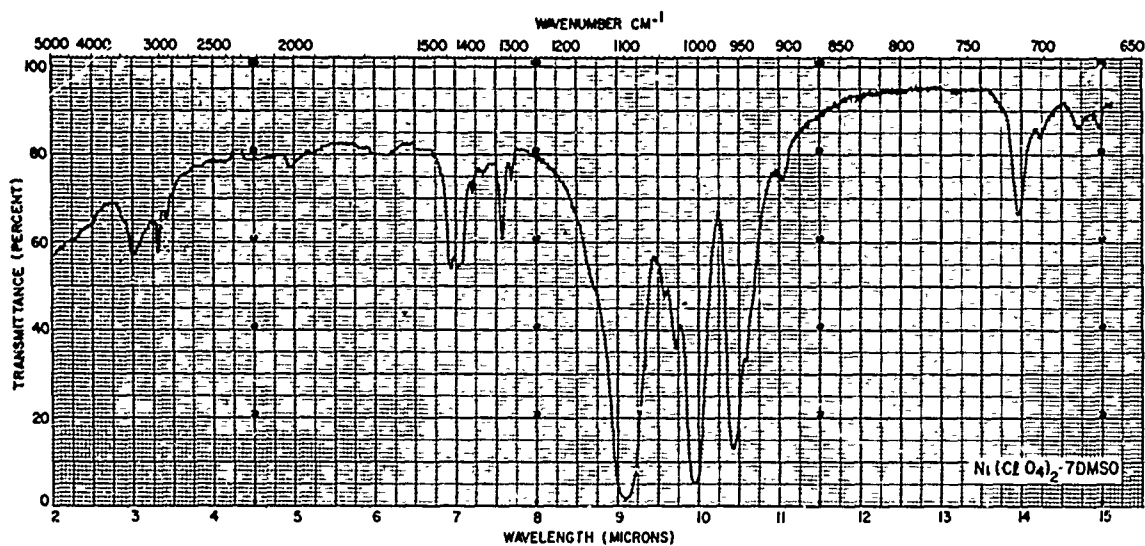
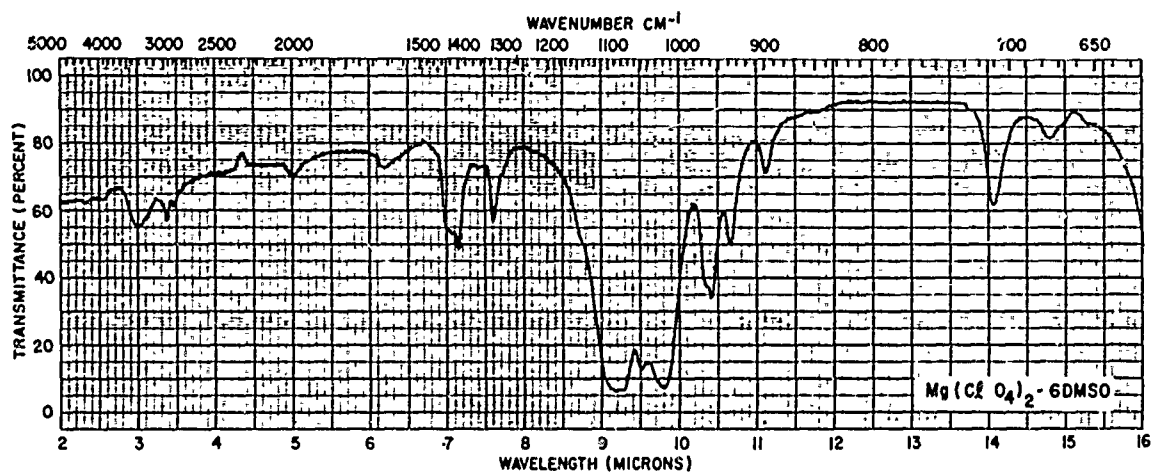
Fig. 2g - Infrared spectrum of $\text{Ni}(\text{ClO}_4)_2 \cdot 7\text{DMSO}$ Fig. 2h - Infrared spectrum of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$

Table 1
Vibrational Modes for Nitrate Groups

Free NO_3^- *			
Assignment	Species	ν (cm^{-1})	
NO stretch	A_1'	ν_1	1050†
Out of plane bend	A_2''	ν_2	831
NO_2 asymmetric stretch	E'	ν_3	1390
NO_2 bend (planar rock)	E'	ν_4	720
Unidentate and Bidentate NO_3^- ‡			
Assignment	Species	ν (cm^{-1})	
		Unidentate	Bidentate
NO_2 symmetric stretch	A_1	ν_1 1290	ν_2 985
NO stretch	A_1	ν_2 1000	ν_1 1630
NO_2 symmetric bend	A_1	ν_3 740	ν_3 785
NO_2 asymmetric stretch	B_1	ν_4 1480- 1550	ν_4 1250
NO_2 asymmetric bend	B_1	ν_5 715	ν_5 750
Out of plane rock	B_2	ν_6 800	ν_6 700

*Ref. 24.

†Inactive in infrared.

‡Ref. 23.

between 715 cm^{-1} and 815 cm^{-1} in the nickel, copper, cobalt, and manganese compounds indicates that the nitrate ion may be coordinated to the metal atoms in these solid complexes. Tetranitrato complexes have been characterized (25,26), but a comparison of the spectrum of the $\text{Co}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ prepared in this work with that of the reported $\text{Co}(\text{NO}_3)_4\text{Co}(\text{DMSO})_6$ cannot be made because of the limited data reported for the latter complex (26). During our preparation of the KBr pellet of $\text{Co}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ the mixture turned blue, indicating a change in the coordination form of the cobalt ion to tetrahedral $(\text{CoBr}_4)^{2-}$ by an anion exchange process (11). Thus our spectrum of the Co complex may have been of a sample which contained cobalt in two different anions. The similarity of the spectra obtained in KBr and in mineral oil indicates that the extent of transformation to tetrabromocobaltate(II) was not great. On the basis of infrared and diffuse reflectance spectra, it has been concluded that $\text{M}(\text{NO}_3)_2 \cdot 3\text{DMSO}$ ($\text{M} = \text{Cu}, \text{Mn}, \text{Zn}$) contains coordinated nitrate (27).

Contact Shifts in DMSO Solutions

The presence of paramagnetic species in a solution can affect the nmr spectrum in several ways (28). Of primary concern here are the so-called contact shifts of ligand resonance lines. These shifts are caused by the distribution from the metal ion to the ligand system of unpaired-electron spin density. Contact shifts have been the subject of numerous investigations, and the field has been reviewed recently (28).

The following equation, derived from a consideration of the Fermi contact term, quantitatively describes the contact shift (28):

$$\frac{\Delta\nu}{\nu} = \frac{-A_n g_{ion} \beta \gamma_e S(S+1)}{\gamma_n 3kT}, \quad (1)$$

where $\Delta\nu (= \Delta\nu_{\text{complex}})$, in Hz, is the contact shift, i.e., the shift of the resonance line from its position in a diamagnetic system; ν , in Hz, is the spectrometer frequency; g_{ion} is the g-factor or spectroscopic splitting factor (29); β is the Bohr magneton; γ_e and γ_n are the gyromagnetic ratios of the electron and proton; S is the total spin of the metal ion; k is the Boltzmann constant; T is the absolute temperature; and A_n is the electron-nuclear hyperfine coupling constant. In π -electron radicals, A_n is related to the unpaired electron density, ρ , at a carbon atom by the expression

$$A_n = Q\rho, \quad (2)$$

where Q is a constant whose value depends on the molecular fragment under consideration (30).

The g-factor can be approximated from the relation

$$g_{ion} = \mu_{eff}/[S(S+1)]^{1/2}. \quad (3)$$

The magnetic moment μ_{eff} should be that measured for the solution, but in this study that obtained from the solid complex has been used. Any differences are not expected to significantly affect the calculated values of the coupling constants.

Rapid ligand exchange in the DMSO solutions has been assumed, since separate peaks are not observed for free and complexed DMSO. In such a system the observed resonance is a weighted average of the shifts of the individual species:

$$\Delta\nu_{obs} = \sum \Delta\nu_i f_i, \quad (4)$$

where f_i is the fraction present as species i . If the chemical shift of free DMSO (2.54 ppm) is taken as zero and the observed shift is measured with respect to free DMSO, then, assuming that there is only one complex species,

$$\Delta\nu_{obs} = \Delta\nu_{\text{complex}} f_{\text{complex}}. \quad (5)$$

From the weights of complex and solvent used, f_{complex} and then $\Delta\nu_{\text{complex}}$ can be calculated (31).

Substituting Eq. (3) for g_{ion} , Eq. (1) can be rearranged to

$$A_n = - \frac{\Delta\nu \gamma_n 3kT}{\nu \beta \gamma_e \mu_{eff} [S(S+1)]^{1/2}}. \quad (6)$$

In Eq. (6), A_n will have units of gauss. It is customary to express A_n in either units of gauss or Hz. To convert gauss to Hz, it is necessary to multiply by $g_e \beta/h$.† Thus, in some previous reports (31) where the coupling constant is given in Hz and is represented by A_n/h , this A_n is a hybrid unit and should be specified as such. It is possible to write Eq. (6) so that A_n will have units of ergs; then the units for A_n/h would be Hz (32). To express A_n in Hz units, Eq. (6) can be written

*We are restricting our discussion to the proton nuclei in the ligand. Other nuclei which are capable of being studied by nmr, e.g., C^{13} , O^{17} , S^{33} , S^{35} , also interact with the metal ion's unpaired electrons.

† $g_e \approx 2$, the g-factor for the free electron.

$$A'_n \text{ (Hz)} = \frac{A_n g_e \beta}{h} = - \frac{\Delta \nu g_e \gamma_n 3kT}{\nu h \gamma_e \mu_{eff} [S(S+1)]^{1/2}} \quad (6a)$$

A more precise method of measuring A_n would be to determine the temperature dependence of $\Delta \nu_{\text{complex}}$. If rapid ligand exchange is occurring at room temperature, then increasing the temperature will provide data for a $\Delta \nu$ vs $1/T$ plot, and A_n could be calculated from the slope of Eq. (1). Decreases in temperature, in a general system, could be made until the half-width of the line started to increase, indicating a change in the rate of exchange; however, the low temperature limit of DMSO solutions is about 10°C . Another check on A_n could possibly be obtained from studies of the complex and various amounts of excess ligand in an inert solvent. However, as noted below, few other solvents suitable for such studies on this system are available.

Table 2 gives the chemical shifts, δ , and line width measurements of the DMSO solutions. The chemical shifts were used to calculate the contact shifts for the complexes (Table 3). However, the chromium and iron complexes, because of their very low solubility, could be studied over only limited concentration ranges; therefore, data on these complexes have been listed for comparison in Table 2, but no coupling constants have been calculated for them.

Table 2
Chemical Shifts and Line Widths of Dimethyl Sulfoxide
Complexes in Dimethyl Sulfoxide Solution

Concentration (moles/liter ⁻¹)	δ (ppm)*	Line Width (Hz)†,‡	Concentration (moles/liter ⁻¹)	δ (ppm)*	Line Width (Hz)†,‡
Cu(NO ₃) ₂ ·3DMSO			Mn(NO ₃) ₂ ·5DMSO·H ₂ O		
0.486	3.19 ± 0.06	62.4	0.478	—	~ 1000
0.243	2.91 ± 0.02	28.2	0.239	—	287
0.122	2.72 ± 0.01	15.9	0.120	3.08 ± 0.05	158
0.061	2.64 ± 0.01	7.2	0.060	2.84 ± 0.02	73.5
0.030	2.59 ± 0.01	3.8	0.030	2.67 ± 0.02	44.7
0.015	2.56 ± 0.01	2.8	0.015	2.61 ± 0.01	20.6
Co(NO ₃) ₂ ·3DMSO			Ni(NO ₃) ₂ ·7DMSO		
0.238	3.51 ± 0.02	4.3	0.111	2.85 ± 0.01	18.5
0.119	3.03 ± 0.03	3.0	0.056	2.69 ± 0.02	9.5
0.060	2.79 ± 0.03	—	0.028	2.61 ± 0.01	5.1
0.030	2.67 ± 0.02	2.0	0.014	2.57 ± 0.01	3.1
0.015	2.60 ± 0.01	1.0			
Fe(NO ₃) ₃ ·6DMSO			Cr(NO ₃) ₃ ·5DMSO		
0.0055	2.55 ± 0.02	2.9	0.0083	2.55 ± 0.02	2.0
0.0027	2.55 ± 0.02	1.5	0.0033	2.55 ± 0.01	1.2
0.0014	2.54 ± 0.02	1.1	0.0017	2.55 ± 0.01	0.8

*Chemical shift in parts per million downfield from an internal TMS reference.

†Line width measured at half peak height.

‡The error in the line width measurements is ±1 Hz for line widths greater than 5 Hz and (+0.5, -0.2) Hz for line widths less than 5 Hz.

Table 3
Calculated Values of Electron-Nuclear Hyperfine
Coupling Constants for DMSO Complex Ions

Ion	$\Delta\nu_{\text{com}}/\nu$ (ppm)	μ_{eff} (B.M.)	S	A_n (gauss)	A'_n (Hz)
$\text{Cu}(\text{DMSO})_6^{+2}$	-3.32	1.95	1/2	3.9×10^{-2}	1.10×10^5
$\text{Ni}(\text{DMSO})_6^{+2}$	-5.97	3.34	1	2.6×10^{-2}	0.72×10^5
$\text{Co}(\text{DMSO})_6^{+2}$	-9.39	5.47	3/2	1.8×10^{-2}	0.50×10^5
$\text{Mn}(\text{DMSO})_6^{+2}$	-10.45	6.09	5/2	1.2×10^{-2}	0.32×10^5

It is possible in certain cases to relate contact shift data to the nature of the bonding between the ligands and the central metal atom and to the mechanism of electron spin delocalization in the ligands (33). If the coordination species is known, molecular orbital theory can be used to determine the energy level diagram which best fits the observed data. Since the work on determining coordination species for the DMSO complexes in DMSO solution has not yet been completed, some general ideas will be developed assuming octahedral coordination for the complex ions, and the results will be compared with similar studies on other systems.

The contact shifts and hyperfine coupling constants for the DMSO complexes are listed in Table 4, along with reported data for aquo and hexamethylphosphoramide $\{[(\text{CH}_3)_2\text{N}]_3\text{PO}$, HMPA} complexes. These three ligands are believed to bond to the metal atom by the donation of the unshared pair of electrons from the oxygen to empty metal d-orbitals, forming a σ -type covalent bond. For σ -type bonding an increase in the number of bonds between the coordinated oxygen of the ligand and the proton whose contact shift is measured should cause a decrease in the contact shift and thus in the coupling constant. Table 4 shows that the prediction is followed for the systems studied. The large values of the contact shift and coupling constant for $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ have been explained using a molecular orbital picture of the aquo complexes (31).

The order of the hyperfine coupling constant in the HMPA complexes was correlated with the stability constants for the salicylaldehyde and malonic acid complexes of

Table 4
Contact Shifts and Hyperfine Coupling Constants for Metal Ions Complexed
with Water, Dimethyl Sulfoxide, and Hexamethylphosphoramide

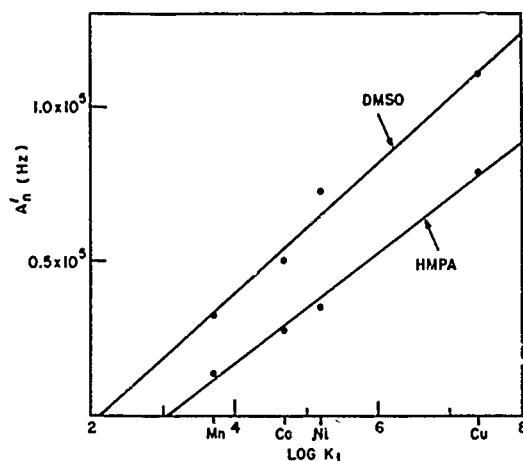
Metal	$\text{M}[\text{OH}_2]_6^{2+*}$		$\text{M}[\text{OS}(\text{CH}_3)_2]_6^{2+}$		$\text{M}[\text{OP}(\text{N}(\text{CH}_3)_2)_3]_6^{2+\dagger}$	
	$\Delta\nu_{\text{com}}/\nu$ (ppm)	A'_n (Hz)	$\Delta\nu_{\text{com}}/\nu$ (ppm)	A'_n (Hz)	$\Delta\nu_{\text{com}}/\nu$ (ppm)	A'_n (Hz)
Cu	-4.3	1.5×10^5	-3.32	1.10×10^5	-2.5	0.78×10^5
Ni	-8.7	1.1×10^5	-5.97	0.72×10^5	-3.3	0.35×10^5
Co	-68.7	4.2×10^5	-9.39	0.50×10^5	-2.8	0.27×10^5
Mn	-168.0	5.9×10^5	-10.45	0.32×10^5	-3.4	0.13×10^5

*Ref. 31.

†Ref. 33.

the metal ions and, hence, with the covalent bonding abilities of the metal ions (33). The DMSO data correlate similarly as shown in Fig. 3 where the coupling constants for the DMSO and HMPA complexes are plotted against the log of the stability constant for the corresponding salicylaldehyde complex (34). Agreement is equally as good when the hyperfine coupling constants are plotted against the stability constants of other oxygen-bonded complexes such as those of malonic acid and oxalic acid. The final test of this relation of the hyperfine coupling to covalent character of the bond would entail a comparison of A_n with the stability constants of the DMSO and HMPA complexes themselves.

Fig. 3 - Relationship between electron-nuclear hyperfine coupling constants, A_n' , for dimethyl sulfide and hexamethylphosphoramide complexes and stability constants of salicylaldehyde complexes

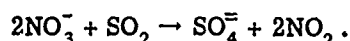


It is surprising that the A_n' 's of the DMSO complexes parallel those of the HMPA complexes, for the metal ions most probably differ in symmetry in the two cases. We believe the DMSO complexes to be octahedral in DMSO solution, whereas the HMPA complexes have been assigned a tetrahedral nature (33). The actual coordination species of the DMSO complexes is under investigation and will be reported at a later time. For the octahedral water complexes Wayland and Rice (31) have proposed an increase in electron delocalization which occurs when unpaired electrons are available in the t_{2g} levels (Mn, Fe, Co) which have π symmetry and interact with π -type molecular orbitals of the water ligands. In tetrahedral complexes the t_{2g} levels can be involved with both σ and π ligand orbitals. Although the environment of the metal ion of DMSO complexes in solution is not yet known, the coupling constant results would indicate that for octahedral Co(II) and Mn(II) DMSO complexes the π contribution of the unpaired t_{2g} electrons is not as large as that found in the corresponding aquo complexes.

The main assumptions employed in the calculation of contact shifts are (a) that the metal ions are octahedrally coordinated in solution, (b) that there is only one complex species, and (c) that exchange of ligand molecules is occurring rapidly. Although the size of DMSO should not prevent hexacoordination, the possibility that other factors, such as anion coordination in solution, may affect the composition of the complex species and thus invalidate assumptions a and b, is currently being investigated. The assumption of rapid ligand exchange is supported by the fact that only one peak is observed in the nmr spectra for each complex at all concentrations. For a system undergoing slow exchange, $Al(ClO_4)_3 \cdot 6DMSO$ in DMSO, a separate peak which broadened with increasing temperature was found downfield from the solvent resonance (35).

Sulfur Dioxide Solutions

Because of exchange between ligand and solvent DMSO molecules a solvent was sought to enable the DMSO complexes to be studied without exchange effects. A chemically inert solvent which was a weaker ligand than DMSO, and which did not interfere with proton nmr measurements, was required. The complexes were insoluble in the common solvents CCl_4 , CHCl_3 , CH_2Cl_2 , and benzene. Another possible choice was SO_2 , since many studies have been successfully run in liquid SO_2 (36,37). Unfortunately, while it is a good nmr solvent and potentially a good solvent for dissolving the complexes, further study revealed that SO_2 is not inert in our systems. Sulfur dioxide apparently reacts with nitrate ion according to the equation



There is some confusion concerning the solubility of nitrate salts in liquid SO_2 . Cady and Taft (38) reported that AgNO_3 and $\text{Ce}(\text{NO}_3)_3$ were soluble in this solvent. Their procedure consisted of checking for any residue remaining after a well-shaken suspension of the salt in the solvent was filtered and the solvent was evaporated from the filtrate. Since no qualitative tests on the residues were reported, there is actually no evidence that the residues were these two nitrates.

The residues may have been sulfates, for Hodgkinson and Young (39) exposed a series of nitrates to SO_2 vapor with the resultant formation of sulfates. Also, Jander (40) reported that a reaction between nitrates and liquid SO_2 formed a great amount of nitrogen oxide which escaped explosively when the reaction tube was opened. Hagenback (41) stated that AgNO_3 became more soluble above room temperature but decomposed and deposited a brown precipitate. Schattenstein and Wiktorow (42) found that $\text{Bi}(\text{NO}_3)_3$, $\text{Ba}(\text{NO}_3)_2$, and LiNO_3 were insoluble, and that the latter two compounds reacted with the solvent. They also reported AgNO_3 and KNO_3 to be soluble to the extent of 0.01 to 0.1% with only the potassium salt reacting with the solvent. The reaction of KNO_3 with SO_2 has been reported to form KNOSO_4 (43). Finally, Jander has stated that the solubility of nitrates in liquid SO_2 cannot be determined because they react with the solvent (44).

Because of the apparent reaction of nitrates with SO_2 we restricted the nmr study of DMSO complexes in this solvent primarily to the nickel compound. Samples of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$ and $\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ in SO_2 were also prepared for comparison. In each of the four samples of $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$ prepared, the compound initially dissolved completely, and within 10 to 20 minutes precipitates formed. Precipitation did not occur in a sample of $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$ (0.027 molal) to which extra DMSO (0.2 molal) had been added. The solutions were yellow-green in color. The nmr spectrum of each of the five samples (under low resolution conditions) showed a broad peak at $\delta = 3.3$ ppm. Six months later, under better resolution, the spectra gave the results shown in Table 5.

In contrast, in yellow solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{DMSO}$, precipitate formation in a 0.112 molal solution did not occur until 1 month had passed, and no precipitate had formed in a 0.03 molal solution after 5 months. The nmr spectrum of the 0.03 molal sample had a broad peak at 3.3 ppm. The data from the spectrum of the 0.112 molal solution taken 4 months after preparation are given in Table 5.

The nmr data for three other systems run for comparison with the metal nitrates are given in Table 6. The $\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$ completely dissolved in liquid SO_2 , and no precipitate formed for over a year. A precipitate was observed in the $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$ solution after 2 years aging at 25°C .

The nmr spectrum of the $\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ solution did not change during a 2-year period, but the spectra of the DMSO and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$ solutions as well as those of the $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$ solutions showed remarkable changes which can be explained only

Table 5
Chemical Shifts of NMR Peaks Found in Aged Liquid Sulfur Dioxide
Solutions of Metal Nitrate-DMSO Complexes

Sample	Molal Concentration	Peak Position (ppm)							
$\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$	0.017	2.11	—	2.67	2.89	2.93	3.27*	—	5.50
$\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$	0.032	—	2.25	2.67	—	2.93	3.27*,†	—	—
$\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$	0.041	—	2.29	2.68	—	2.93	3.29*,†	—	5.40
$\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$	0.063	—	—	—	—	2.93	3.29*,†	—	—
$\text{Ni}(\text{NO}_3)_2 \cdot 4\text{DMSO}$ plus excess DMSO	0.027 complex plus 0.205 DMSO excess	—	—	2.58	—	—	3.31	3.79*	—
$\text{Fe}(\text{NO}_3)_3 \cdot 6\text{DMSO}$	0.112	—	—	2.70	2.85 (broad)	—	3.31	—	5.50 (very broad)

*Most intense peak.

†Half-width ~ 7 Hz.

Table 6
NMR Data for Methyl Peaks of DMSO, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$
and $\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ in Liquid Sulfur Dioxide

Sample	Molal Concentration	δ (ppm)	Line Width (Hz)
DMSO	0.67	2.640 ± 0.005	0.4
$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$	0.09	2.766 ± 0.005	0.6
$\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$	0.113	10.1 ± 0.1	82.0

by postulating a reaction between the SO_2 solvent and DMSO. No change was found in the control blank, TMS in SO_2 , so this system appears to be stable. In addition to the spectral changes, the color of the DMSO- SO_2 solution had changed from colorless to slightly yellow. Also, a second liquid phase, heavier than liquid SO_2 , was observed. A second phase was also found in the nickel nitrate with excess DMSO. The reaction between liquid SO_2 and DMSO is currently being investigated and will be the subject of a future report.

SUMMARY AND FUTURE PLANS

Although DMSO complexes form readily, in many cases the complex actually isolated depends strongly on the manner of preparation. Among the transition metal nitrates, those of Mn, Co, and Cu have a tendency to form tetranitrato-metal anions, perhaps utilizing the bidentate capabilities of the nitrate ion to form octahedral anions. The nitrates of iron and chromium form DMSO complexes which are relatively insoluble in DMSO.

The infrared data from the solid compounds indicate bonding of the ligand to the metal through the oxygen atom. The nmr contact shift calculations indicate that electron delocalization through a π -orbital system is not as extensive as that which occurs in the aquo complexes of the same metal ions. This finding is based on the assumption that the metal ions exhibit octahedral coordination in DMSO solution. The coordination state of the metal ions in solution is being investigated by magnetic susceptibility measurements and ultraviolet, visible, and near-infrared spectroscopy.

Liquid SO_2 was found to be a poor solvent for the DMSO complexes studied here because of the reaction between nitrates and SO_2 . Studies of this reaction and of the reaction between liquid SO_2 and DMSO will be carried out as time allows.

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Appendix A

A LIST OF METHODS USED TO STUDY DIMETHYL SULFOXIDE COMPLEXES

Although this report is not a review on DMSO complexes, it seems appropriate to list the various approaches used in other studies of these complexes. Insofar as infrared spectroscopy is concerned, Appendix B gives the references for those cases where the S-O stretching frequency was reported. The references listed below under "Infrared Spectroscopy" are those in which these frequencies are discussed or where some other aspects of the spectra were of interest. Although not all references to each technique are given, it is believed that all methods employed so far are represented.

Infrared Spectroscopy 13,17,22,A1-A3	Polarography A20,A21
Far Infrared Spectroscopy A4,A5	Dipole Moment Measurements A22
Ultraviolet Spectroscopy 26,27,A2,A6-A8	Differential Thermal Analysis and Thermogravimetric Analysis 18,21,A1,A23,A24
Fluorescence Spectroscopy 19	Magnetic Susceptibility 26,A2,A6,A25
X-ray Spectroscopy 14,A10-A12	Conductivity A2,A25,A23,A26
Electron Spin Resonance A13,A14	Conductimetric Titration A27
Nuclear Magnetic Resonance 35,A15-A19	Oscillometric Titration A28

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Appendix B

LIST OF DIMETHYL SULFOXIDE COMPLEXES

The following list includes essentially all the DMSO complexes reported up to December 1966. The S-O stretching frequencies have been given for those complexes for which they were reported. The complexes are listed according to Groups of the Periodic Table. Not included are a number of charge transfer complexes and some ionic-type compounds.

The authors would appreciate having any omissions brought to their attention.

Group I A

<u>Complex</u>	<u>ν_{S-O} (cm⁻¹)</u>	<u>Reference</u>
LiCl·DMSO		B1, B2
LiBr·3DMSO		B1
LiI·3DMSO		B1
LiClO ₄ ·3.5DMSO		B1
Li ₂ SO ₄ ·0.5DMSO		B1
NaBr·2DMSO		B1
NaI·3DMSO		B1
NaClO ₄ ·3DMSO		B1
Na ₂ SO ₄ ·0.66DMSO		B1
KCl·0.66DMSO		B1
KI·2DMSO		B1
KNCS·DMSO		B3

Group I B

CuCl ₂ ·DMSO	987	13
CuCl ₂ ·2DMSO	923, 987	11, 12, 13, 17, A23, B2
CuBr ₂ ·2DMSO	911, 989	11, 12, 13, 17
CuBr ₂ ·3DMSO		11, B2
Cu(ClO ₄) ₂ ·4DMSO	940, 986	11, 13, 17
Cu(ClO ₄) ₂ ·9DMSO		B2
CuSO ₄ ·2DMSO		11
Cu(NO ₃) ₂ ·2DMSO		11
Cu(NO ₃) ₂ ·3DMSO		27, this work
Cu(OAc) ₂ ·DMSO		A23

Group I B (cont'd)

Complex	ν_{S-O} (cm ⁻¹)	Reference
$[Cu(CH_3C_5H_4NO)(DMSO)Br_2]_n$		B4
$Cu[N(CN)_2]_2 \cdot 2DMSO$		A25
$Cu[C(CN)_3]_2 \cdot 6DMSO$		A25
$Cu[C(CN)_3]_2 \cdot DMSO$		A25
$AgBF_4 \cdot DMSO$		B5

Group II A

$Mg(ClO_4)_2 \cdot 6DMSO$	10
$Mg(NO_3)_2 \cdot 6DMSO$	27

Group II B

$ZnCl_2 \cdot 2DMSO$	952	11,17
$ZnBr_2 \cdot DMSO$	942	11,17
$Zn(NO_3)_2 \cdot 2DMSO$		11
$Zn(ClO_4)_2 \cdot 6DMSO$	956	11,17
$Zn(ClO_4)_2 \cdot 4DMSO$	1018	13
$Zn[N(CN)_2]_2 \cdot 0.5DMSO$		A25
$Zn[C(CN)_3]_2 \cdot 6DMSO$		A25
$Zn(NO_3)_2 \cdot 8DMSO$		27
$Zn(NO_3)_2 \cdot 3DMSO$		27
$CdCl_2 \cdot DMSO$	950, 991	11,13,17
$CdBr_2 \cdot DMSO$	996	13
$Cd[N(CN)_2]_2 \cdot 2DMSO$		A25
$Cd[C(CN)_3]_2 \cdot 6DMSO$		A25
$HgCl_2 \cdot DMSO$	1005	13
$Hg(ClO_4)_2 \cdot 6DMSO$		B6
$Hg(SCN)_2 \cdot 2DMSO$	1027	12
$R_2Hg \cdot DMSO$ and $R_2Hg \cdot 2DMSO$ benzene solution (R = fluorinated alkyl groups)		A28

Group III A

$BF_3 \cdot DMSO$	938	6,11,A12
$1,6-(CH_3)_2SB_{10}H_8OS(CH_3)_2$		B7
$H_2B_{10}Cl_{10} \cdot 4DMSO$		B8
$B_{10}H_{12} \cdot 2DMSO$		B9
$[BH_2 \cdot 2DMSO]^+ Cl^-$		B10
$[BH_2 \cdot 2DMSO]^+ BH_4^-$		B10
$AlCl_3 \cdot 6DMSO$	1009	11,13

Group III A (cont'd)

<u>Complex</u>	<u>ν_{S-O} (cm⁻¹)</u>	<u>Reference</u>
AlCl ₃ ·2DMSO		B2
Al(NO ₃) ₃ ·6DMSO		11
Al(ClO ₄) ₃ ·6DMSO		A21
Ga(ClO ₄) ₃ ·6DMSO	993	13
InCl ₃ ·3DMSO	962, 950, 932	B11, B12
InBr ₃ ·3DMSO	995, 960	A24
InI ₃ ·2DMSO	940, 960, 980	A24
In(NO ₃) ₃ ·6DMSO	945	B13
In(ClO ₄) ₃ ·6DMSO	950	B14
TlCl ₃ ·2DMSO	930	B15
TlBr ₃ ·2DMSO	930	B12

Group IV A

SiF ₄ ·2DMSO	~950	A15, B16
GeF ₂ ·DMSO	1020	B17
GeF ₄ ·2DMSO		A15
GeCl ₄ ·2DMSO	894	B18
SnF ₂ ·DMSO		B17
SnF ₄ ·2DMSO		A15
SnCl ₂ ·1.5DMSO		B18
SnCl ₂ ·2DMSO	920	B19
SnCl ₄ ·2DMSO	920	6, 11, 17, A4, B19
SnBr ₄ ·2DMSO	911	6, A4
SnI ₄ ·2DMSO	924	6
MeSnCl ₃ ·2DMSO	928	B18, B20
Me ₂ SnCl ₂ ·2DMSO	944	B18
Me ₃ SnCl·DMSO	958	B18
Me ₂ Sn(NO ₃) ₂ ·1.5DMSO	954	B21
PhSnCl ₃ ·2DMSO	911	B18
Ph ₂ SnCl ₂ ·2DMSO	948	B18, B20
Ph ₃ SnCl·DMSO	954	B18
Ph ₃ SnSCN·DMSO		B22
(p-ClPh) ₃ SnCl·DMSO		B22
(Cyclohexyl) ₂ SnCl ₂ ·2DMSO		B20
PbCl ₂ ·DMSO	987	13, B3
PbBr ₂ ·DMSO	978	13

Group IV A (cont'd)

<u>Complex</u>	<u>ν_{S-O} (cm⁻¹)</u>	<u>Reference</u>
PbI ₂ ·2DMSO		B3
Pb(ClO ₄) ₂ ·3DMSO	986	13
Ph ₂ PbCl ₂ ·2DMSO	945	B18,B23
Ph ₂ PbBr ₂ ·2DMSO		B23

Group IV B

TiF ₄ ·2DMSO		A15
TiCl ₄ ·2DMSO		B2
TiCl ₄ ·11DMSO	950	B24
TiBr ₄ ·11DMSO	950	B24
TiO(ClO ₄) ₂ ·5DMSO	934	18
(EtO) ₃ TiCl·DMSO		B25
ZrF ₄ ·2DMSO		A15
ZrCl ₄ ·9DMSO	950	B24
ZrBr ₄ ·10DMSO	910	B24
ZrO(ClO ₄) ₂ ·8DMSO	938	18
ZrO(ClO ₄) ₂ ·6DMSO	1148	18
HfCl ₄ ·9DMSO	920	B24
HfBr ₄ ·10DMSO	920	B24

Group V A

PF ₅ ·DMSO		A16
PF ₆ ⁻ Me ₂ SOH ⁺		B26
SbCl ₃ ·2DMSO		B27
SbCl ₅ ·DMSO		B2,B27
SbONO ₃ ·DMSO		B28
Bi(NO ₃) ₃ ·3DMSO		B28

Group V B

VOCl ₂ ·3DMSO	1015	A2,B29
VOBr ₂ ·5DMSO		B29
VOSO ₄ ·3DMSO		B29
VO(ClO ₄) ₂ ·5DMSO		B29
[V(CO) ₆] ₂ V(DMSO) ₄		B30
NbF ₅ ·2DMSO	940	B31
NbOCl ₃ ·2DMSO	915	B32
Nb ₄ Br ₃ O ₆ ·6DMSO*	940	L32

*Approximate composition of polymeric material.

Group V B (cont'd)

<u>Complex</u>	<u>ν_{S-O} (cm⁻¹)</u>	<u>Reference</u>
Nb ₄ Br ₈ O ₆ ·8DMSO*		B32
TaF ₅ ·2DMSO	878	B31
Ta ₂ O ₆ Cl ₃ ·3DMSO*	940	B32
Ta ₃ O ₄ Cl ₇ ·5DMSO*		B32
Ta ₂ BrO ₅ ·3DMSO*	935	B32
Ta ₃ Br ₇ O ₄ ·5DMSO*		B32

Group VI B

CrCl ₃ ·3DMSO		11,A8
CrCl ₃ ·4DMSO	935	17
CrCl ₃ ·5DMSO		B2
CrBr ₃ ·6DMSO		B2
Cr(NO ₃) ₃ ·5DMSO		this work
Cr(NO ₃) ₃ ·6DMSO		B2
Cr(ClO ₄) ₃ ·6DMSO	928	11,17,A7,B2
Cr(CO) ₅ ·DMSO		A22
C ₆ H ₆ Cr(CO) ₂ DMSO	1086	16,B33
p(MeO ₂ S) ₂ C ₆ H ₄ Cr(CO) ₂ DMSO		B33
1,3,5 Me ₃ C ₆ H ₃ Cr(CO) ₂ DMSO	1078	16,B33
(CH ₃) ₆ C ₆ Cr(CO) ₂ DMSO	1068	16
(CO ₂ CH ₃) ₂ C ₆ H ₄ Cr(CO) ₂ DMSO	1098	16
K[Cr(C ₂ O ₄) ₂ (DMSO) ₂]·2DMSO		B34
Mo ₆ Cl ₁₂ ·2DMSO	927	B35
Mo ₆ Cl ₈ (ClO ₄) ₄ ·6DMSO	930	B35
Mo ₆ Cl ₈ (CH ₃ SO ₃) ₄ ·2DMSO		B35
MoOCl ₃ ·2DMSO	1032, 999	B36,B37
MoO ₂ Cl ₂ ·2DMSO	1030, 986	B36
MoF ₄ ·2DMSO		A15
4MoO ₃ ·5DMSO		B28
Mo(CO) ₃ ·3DMSO		B38
W(CO) ₅ DMSO		A22

Group VII B

MnCl ₂ ·3DMSO	950	11,12,17,B2
MnBr ₂ ·2DMSO		11

*Approximate composition of polymeric material.

Group VII B (cont'd)

<u>Complex</u>	<u>ν_{S-O} (cm⁻¹)</u>	<u>Reference</u>
MnBr ₂ ·3DMSO·6H ₂ O	952	11,17
MnBr ₂ ·6DMSO		B2
MnI ₂ ·4DMSO		11
MnI ₂ ·6DMSO		B2
Mn(NO ₃) ₂ ·6DMSO		27,B2
Mn(NO ₃) ₂ ·5DMSO·H ₂ O		this work
Mn(NO ₃) ₂ ·3DMSO		27, this work
Mn(ClO ₄) ₂ ·3DMSO·4H ₂ O	954	11,17
Mn(ClO ₄) ₂ ·6DMSO	955, 1001	11,13,17,A7,B2
Mn[N(CN) ₂] ₂ ·2DMSO		A25
Mn[C(CN) ₃] ₂ ·6DMSO		A25
[Mn(CO) ₄ ·2DMSO]Cl		B39
[Mn(CO) ₄ ·2DMSO]Br		B39
[Mn(CO) ₄ ·2DMSO]I		B39
C ₅ H ₅ Mn(CO) ₂ DMSO	1101	15,B40
C ₅ H ₅ Mn(CO)·2DMSO		B40
CH ₃ C ₅ H ₄ Mn(CO) ₂ DMSO		A22
Re ₃ Cl ₃ (AsO ₄) ₂ ·2DMSO		B41
Re ₃ Cl ₃ (AsO ₃) ₂ ·2DMSO		B41
Re ₃ Br ₃ (AsO ₄) ₂ ·3DMSO	925	B41
Re ₃ Br ₃ (AsO ₃) ₂ ·2DMSO		B41
Re ₃ Br ₃ (PO ₄) ₂ ·2DMSO		B41
ReOCl ₃ PPh ₃ ·DMSO	1138, 1129	20
ReO ₂ Cl·2DMSO	907, 895	20
ReOBr ₃ PPh ₃ ·DMSO	1131, 1122	20

Group VIII

FeCl ₃ ·2DMSO	933, 988	11,13,17
FeCl ₃ ·3DMSO		A23
FeCl ₃ ·4DMSO		B2
FeBr ₃ ·6DMSO		11
FeI ₂ ·4DMSO	937	17
Fe(NO ₃) ₃ ·6DMSO		B2,B42, this work
Fe(ClO ₄) ₂ ·6DMSO	989	13
Fe(ClO ₄) ₃ ·6DMSO	988	13,B2
Fe(ClO ₄) ₃ ·7DMSO	940	11,17

Group VIII (cont'd)

<u>Complex</u>	<u>ν_{S-O} (cm⁻¹)</u>	<u>Reference</u>
[Fe(DMSO) ₆][Fe ₄ (CO) ₁₃]		B43
CoCl ₂ ·3DMSO	950, 999	11,12,13,17,A23,B2
CoBr ₂ ·3DMSO	951	11,17
CoBr ₂ ·8DMSO		B2
CoI ₂ ·3DMSO	951	12,17,A6
CoI ₂ ·6DMSO	948	11,12,17,B2
Co(NO ₃) ₂ ·3DMSO		26, this work
Co(NO ₃) ₂ ·4DMSO		A23
Co(NO ₃) ₂ ·8DMSO		27,B2
Co(ClO ₄) ₂ ·6DMSO	956, 1000	11,13,17,A7
Co(ClO ₄) ₂ ·8DMSO		B2
Co[N(CN) ₂] ₂ ·2DMSO		A25
Co[C(CN) ₃] ₂ ·6DMSO		A25
Co(SCN) ₂ ·3DMSO	950	17,A6
Co(SCN) ₂ ·4DMSO	953	17,A6
[Co(en) ₂ (DMSO) ₂](ClO ₄) ₃		B44
[Co(en) ₂ (DMSO)Cl]NO ₃ ClO ₄		B45
[Co(en) ₂ (DMSO)Br](ClO ₄) ₂		B46
[Co(en) ₂ (DMSO)Cl](ClO ₄) ₂		B47
(CoSaEn) ₂ O ₂ ·2DMSO		B48
(CoSaEn) = N,N'-ethylenebis(salicylideneiminato)Cobalt(III)		
RhCl ₃ ·3DMSO		A5
RhI ₃ ·3DMSO		A5
Rh(CO)Cl·2DMSO		B49
Rh(OOCCH ₃) ₂ ·2DMSO	1086	19
IrCl ₃ ·3DMSO(cis and trans)		B50
HfCl ₄ ·2DMSO(cis and trans)		B50
NH ₄ ⁺ , K ⁺ and isoquinolium salts of HfCl ₄ ·2DMSO		B50
NiCl ₂ ·3DMSO	940, 1004	11,12,13,17,A23,B2
NiBr ₂ ·3DMSO	951	17,A6
NiBr ₂ ·4DMSO	956	17,A6
NiBr ₂ ·6DMSO	957	17,A6
NiBr ₂ ·8DMSO		B2
NiI ₂ ·4DMSO	930	17,A6
NiI ₂ ·6DMSO		A6,B2
Ni(NO ₃) ₂ ·4DMSO		A6, this work

Group VIII (cont'd)

<u>Complex</u>	<u>ν_{S-O} (cm⁻¹)</u>	<u>Reference</u>
Ni(NO ₃) ₂ ·7DMSO		this work
Ni(NO ₃) ₂ ·8DMSO		27,B2
Ni(ClO ₄) ₂ ·6DMSO	955, 1002	11,13,17,A7
Ni(ClO ₄) ₂ ·7DMSO		this work
Ni(ClO ₄) ₂ ·8DMSO		B2
Ni[N(CN) ₂] ₂ ·2DMSO		A25
Ni[C(CN) ₃] ₂ ·8DMSO		A25
Ni[C(CN) ₃] ₂ ·DMSO		A25
[Ni(DMSO) ₆][B(C ₆ H ₅) ₄] ₂	1000	12
Ni(SCN) ₂ ·4DMSO		A6
PdCl ₂ ·2DMSO	1116, 1118	11,13,17
PtCl ₂ ·x DMSO	1110	13
PtCl ₂ ·2DMSO	1134	13,17
Rare Earths		
(C ₁₅ H ₁₁ O ₂) ₃ Eu·3DMSO	1044	B51
LaCl ₃ ·4DMSO	1010	A26
CeCl ₃ ·4DMSO		A26
PrCl ₃ ·4DMSO		A26
NdCl ₃ ·4DMSO		A26
SmCl ₃ ·4DMSO		A26
GdCl ₃ ·4DMSO	1012	A26
YCl ₃ ·3DMSO	1010	A26
La(NO ₃) ₃ ·4DMSO	1010	B52
Ce(NO ₃) ₃ ·4DMSO		B52
Pr(NO ₃) ₃ ·4DMSO		B52
Nd(NO ₃) ₃ ·4DMSO		B52
Sm(NO ₃) ₃ ·4DMSO		B52
Gd(NO ₃) ₃ ·4DMSO		B52
Y(NO ₃) ₃ ·3DMSO	1011	B52
La(ClO ₄) ₃ ·8DMSO	998	B53
Ce(ClO ₄) ₃ ·8DMSO	992	B53
Pr(ClO ₄) ₃ ·8DMSO	993	B53
Nd(ClO ₄) ₃ ·8DMSO	996	B53
Sm(ClO ₄) ₃ ·7DMSO	995	B53
Gd(ClO ₄) ₃ ·7DMSO	998	B53

Rare Earths (cont'd)

<u>Complex</u>	<u>ν_{S-O} (cm⁻¹)</u>	<u>Reference</u>
Y(ClO ₄) ₃ ·7DMSO	1000	B53
Actinide Series		
ThCl ₄ ·5DMSO	942	A1
ThBr ₄ ·6DMSO	948	A1
Th(NO ₃) ₄ ·6DMSO		11
ThO(ClO ₄) ₂ ·12DMSO	946	18
ThO(ClO ₄) ₂ ·6DMSO	1144	18
UCl ₄ ·3DMSO	947	A1
UCl ₄ ·4DMSO	935	B54
UBr ₄ ·6DMSO	937	A1
UO ₂ Cl ₂ ·3DMSO	995	B55,B56
UO ₂ Br ₂ ·DMSO		A1
UO ₂ Br ₂ ·4.5DMSO	995	B55,B56
UO ₂ (NO ₃) ₂ ·2DMSO		11
UO ₂ (NO ₃) ₂ ·4.5DMSO		B57
UO ₂ (ClO ₄) ₂ ·4DMSO	1152	21
UO ₂ (ClO ₄) ₂ ·4.6DMSO		B57
UO ₂ (ClO ₄) ₂ ·5DMSO	941	21,B58

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13. ABSTRACT Dimethyl sulfoxide [(CH ₃) ₂ SO, DMSO] complexes of Cr(NO ₃) ₃ , Mn(NO ₃) ₂ , Fe(NO ₃) ₃ , Co(NO ₃) ₂ , Ni(NO ₃) ₂ , Cu(NO ₃) ₂ , Ni(ClO ₄) ₂ , and Mg(ClO ₄) ₂ were prepared and investigated using infrared and nuclear magnetic resonance (nmr) spectroscopy. The infrared data indicate that the ligand forms a coordinate bond to the metal through the oxygen atom in all of the complexes, and that the tetranitrato-metal anion is present in Mn(NO ₃) ₂ ·3DMSO, Co(NO ₃) ₂ ·3DMSO, and Cu(NO ₃) ₂ ·3DMSO. The nmr spectra of Mn(NO ₃) ₂ ·3DMSO, Co(NO ₃) ₂ ·3DMSO, Ni(NO ₃) ₂ ·4DMSO, and Cu(NO ₃) ₂ ·3DMSO in DMSO solutions have been analyzed in terms of contact shifts, $\Delta\nu_{\text{complex}}$, and electron-nuclear hyperfine coupling constants, A_n' . The results correlate with the covalent-bond strengths of the metal atoms and fit a model for electron-spin delocalization via the σ -bond system of the complexes. Attempts to utilize liquid SO ₂ as a solvent for the nmr studies were hampered by a reaction between SO ₂ and the nitrate ion. Literature references to DMSO complexes and to techniques used in their study are presented in two appendixes.			

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